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Hydrometallurgical recovery of cadmium and nickel from spent Ni–Cd batteries

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Abstract

The paper is concerned with a simple hydrometallurgical method for the selective recovery of cadmium and nickel from spent Ni–Cd batteries. The following consecutive stages are proposed: dismantling, leaching in sulphuric acid, cadmium electrowinning, Fe^{3+} removal and nickel electrowinning. The influence of H_2O_2 addition to the leaching solution on the efficiency of the dissolution process was investigated. The electrowinning of cadmium was carried out at various pH and current densities (100 and 400 A/m^2). Fe^{3+} ions were removed from the bath by hydroxide precipitation. Nickel electrolyses were conducted at pH of 9 and two current densities (100 and 400 A/m^2). Concentrations of Ni^{2+}, Cd^{2+} and Fe^{3+} ions as well as cathode potentials and electrolysis voltages were monitored during the electrowinning. Efficiencies of leaching and electrolysis were calculated. Final products were metals of high purity (98–100% Cd, 98–99% Ni). Maximum total recoveries of cadmium and nickel from spent Ni–Cd batteries were 92% and 67%, respectively. A preliminary assessment of an economic viability of the proposed treatment was undertaken.
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1. Introduction

At the present time economical and environmental requirements impose the development of effective and inexpensive methods for the recovery of valuable metals from secondary sources. In this respect, an unusual place among non-ferrous metals belongs to cadmium. Over the past 40 years the main cadmium application has changed from coatings to portable Ni–Cd batteries (Plachy, 2003). However, due to its high toxicity the public have been pressing to reduce or even eliminate the use of cadmium in many countries. Although the consumption of cadmium in everyday life seems to decrease slowly, potential new applications as thin photovoltaic films of CdSe and CdTe appear useful for solar energy generation (Pandey et al., 2000).

The declining production of cadmium from primary sources in a number of developed countries (mainly in Europe) is offset by the increased production in some Asian states. Moreover, the statistics have indicated an increase in the consumption since 1992, especially due to the continuing strength of the Chinese market for Ni–Cd batteries (Morrow, 2003). In the future, it is also quite possible that the growing markets would emerge in other developing countries.

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This situation has resulted in increasing emphasis on the production of cadmium from secondary sources and the recycling of spent batteries is a young and growing industry. Recycling Ni–Cd batteries is essential not only for environmental reasons (Rydh and Karlström, 2002; Rydh and Svärd, 2003), but for economic ones as well. The vast number of applications of the alkaline rechargeable Ni–Cd cells (Putois, 1995) provides a well-stocked source of metals, since the annual supply of spent batteries corresponds to thousands of tons of cadmium and nickel (Ni–Cd cells consist of 12–15% Cd and 15–20% Ni (Rydh and Svärd, 2003)) which are currently discarded to landfill. Several countries in Europe, Asia and South America have already explored the possibilities of establishing labelling, collection and recycling programs for Ni–Cd batteries, while others are in the organization stage (David, 1995; Bernardes et al., 2004). Currently, the industrial treatment of spent Ni–Cd batteries is mostly pyrometallurgical, for instance Inmetco (USA), Accurec (Germany), SabNife (Sweden) or Snam-Svam (France). Some hydrometallurgical methods are also employed, e.g. Batenus (Germany) or TNO (Holland) processes. These are based mainly on solvent extraction followed by electrowinning, ion exchange or membrane technology.

Various authors investigated in details the individual stages of the hydrometallurgical treatment. Studies of acidic leaching (Yang, 2003; Nogueira and Margarido, 2004; Pietrelli et al., 2005), solvent extraction of cadmium and nickel ions (Galán et al., 1998; Nogueira and Delmas, 1999; Reddy et al., 2006), electrodeposition of cadmium (Bartolozzi et al., 1995; Yang, 2003; Freitas and Rosalem, 2005) have all been reported. Some biohydrometallurgical methods to treat spent batteries have also been proposed (Cerruti et al., 1998; Zhu et al., 2003). Most of the research work focused on the recovery of metals from the separated streams. Moreover, sulphate or carbonate was proposed usually as the final nickel product. In the present work, the hydrometallurgical route for the recovery of metallic cadmium and nickel was developed.

Electrolysis is one of the simplest methods for the production of high purity metals. However, purity often decreases when the electrolyte contains several metallic cations and codeposition occurs. Some tests on the selective electrodeposition of cadmium and nickel were carried out by Bartolozzi et al. (1995). They showed the possibility of electrowinning cadmium from an acidic solution (pH 5) in the presence of nickel ions. The electrolysis stage was preceded by the precipitation of Fe^{3+} in the form of hydroxide. The authors did not mention any decrease of Cd^{2+} and Ni^{2+} ions concentration in the solution after iron removal, despite of the

fact that $Fe(OH)_3$ offers good adsorption features and high losses of valuable metals during precipitation are observed (Han et al., 1982). The aim of this work is to study the ability of the selective electrowinning of cadmium and nickel directly from the acid solution after leaching spent Ni–Cd batteries.

2. Experimental

Two brands of spent Ni–Cd batteries (AA-size-Sony, Saft) with a mean weight of 32 g were used in the experiments. The batteries were dismantled into the separate components of the cell. The steel case was opened manually and the rolled electrodes with the polymeric separators and the active cell material were extracted carefully. The electrodes (anodes and cathodes) were perforated steel plaques. Each electrode was covered by proper active electrode material: the anode (negative electrode) by cadmium hydroxide, while the cathode (positive electrode) by nickel hydroxide. The synthetic separators impregnated with potassium hydroxide solution (30%) were insulators between the two electrodes (Pietrelli et al., 2005).

The components of the random specimen were disaggregated and weighed. The active electrode materials were physically removed from the electrode plaques, but they were not cleaned chemically from the material strongly adhered to the surface of the electrode. Each component of the cell was dissolved with hot HNO_3 (1:1) solution and concentrations of Ni^{2+}, Cd^{2+} and Fe^{3+} ions were determined by atomic absorption spectrophotometry (Solaar AA Spectrometer). The mixture of the active electrode materials was analyzed additionally by means of a scanning microscope (Hitachi) with EDS analyser (Noran).

The recovery of cadmium and nickel was carried out using the scheme presented in Fig. 1. The cells devoid of the steel case and the polymeric separators were used. Weighed amounts (20 g) of the mixture of the active electrode materials and the metallic electrodes were leached with 500 cm^3 of 20% H_2SO_4 (s:l ≈ 1:30 w/w). Three series of experiments with various dosages of 30% H_2O_2 (details are summarized in Table 1) were conducted. The leaching was carried out at 80 °C (the raw material was dropped into the warm solution) for 5 h. The solution was agitated periodically (continuous agitation of the solution with magnetic or mechanical stirrer was impossible mainly due to the magnetic properties of the leached material and the construction of the vessel). Liquor samples were taken periodically and the concentrations of Ni^{2+}, Cd^{2+} and Fe^{3+} ions were determined by AAS. At the end of leaching the solution was filtered. The solid residues were divided
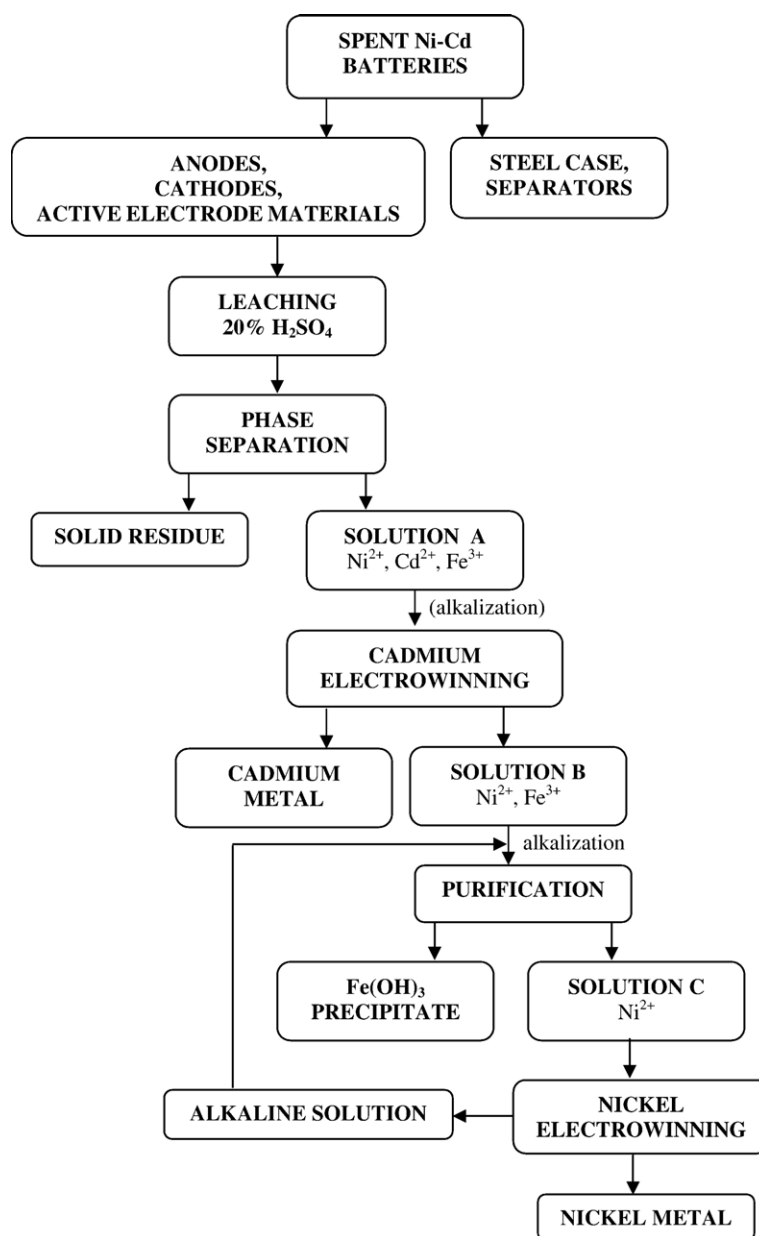
Fig. 1. Scheme of the hydrometallurgical treatment of spent Ni–Cd batteries.

manually into two fractions to separate the scraps of the metallic perforated plaques, then washed with distilled water and dissolved in hot HNO_3 (1:1) solution. The washings were added to the filtrate, and the volume of the solution was reduced to 500 cm^3 by evaporation (SOLU-TION A). Both sulphate and nitrate solutions were analysed for Ni^{2+}, Cd^{2+} and Fe^{3+} ions.

Electrowinning was conducted directly from the sulphate solution at room temperature. The details of the process are presented in Table 2. The electrolysis was carried out in 200 cm^3 of SOLUTION A with cadmium

electrodeposition conducted at either natural pH or pH 1 (after adjustment using concentrated NaOH). After recovery of cadmium, the remaining solution (SOLU-TION B) was neutralised to pH 3 with NaOH where Fe^{3+}

Table 1
Composition of leaching solutions

Series	Composition of the solution
L-I	20% H_2SO_4
L-II	20% H_2SO_4+5 cm^3 30% H_2O_2 (added at the beginning)
L-III	20% H_2SO_4+110 cm^3 30% H_2O_2 (added periodically)

Table 2
Conditions of the electrowinning of metals

Series	Metal	Initial volume of solution, cm^3	Initial pH	Current density, A/m^2
E-I	Cd	200	1	100
	Ni	500	9	
E-II	Cd	200	1	400
	Ni	500	9	
E-III	Cd	200	−1	400
	Ni	1000	9	

precipitated and then raised to pH 9 with 25% NH_3. After filtration to remove the iron, the volume of the solution increased to 500 cm^3 (or 1 dm^3), and the pH was 9 (SOLUTION C).

The electrolyses were carried out with a stainless steel plate as the cathode substrate (20 cm^2) and a platinum net as the anode. The electrolyte was agitated with a magnetic stirrer with rotation rate of 180 rpm. During the process, the samples of the electrolyte were taken and concentrations of Ni^{2+}, Cd^{2+} and Fe^{3+} ions were determined by AAS. Cathodic deposits were stripped from the substrate with HNO_3 solution to determine their composition. Throughout the electrolysis the cathode potential was monitored using a saturated calomel electrode as the reference. The voltage of the electrolysis was controlled as well. A copper coulometer was included in the electric circuit.

3. Results and discussion

3.1. Characterization of material

Two specimens of spent Ni–Cd batteries (B-1, B-2) were divided into the individual components. On average, the AA Ni–Cd battery consisted of (in wt.%): $55.4 \pm 1.4\%$ active electrode material, $22.5 \pm 1.0\%$ anode, $11.4 \pm 1.4\%$ cathode and $10.7 \pm 1.0\%$ separators. The calculated values do not include the steel case.

Table 3 shows the chemical compositions of the components of the cell. It was found that cadmium was the main constituent of the anode, nickel was present in both the active electrode materials and the cathode. Iron was present in both electrodes. Detailed analysis of dry active electrode materials from the cell showed the presence of potassium $63.6 \pm 1.1\%$, nickel $14.9 \pm 1.0\%$, cadmium $2.1 \pm 1.0\%$ and oxygen $17.8 \pm 1.0\%$ (the cell active material represents a mixture of hydroxides).

3.2. Acidic leaching

The major components leached with the acid solution were metals (the electrodes) and hydroxides (the electrode active materials). Good solubility of the hydroxide phase was expected. The metallic phases were more resistant to 20% H_2SO_4 and required an additional oxidant. Hence, three series of the experiments with various dosages of 30% H_2O_2 were conducted. Fig. 2 shows the influence of the time on the percentage of metal leached. After 0.5 h considerable amounts of metal ions were present in the electrolyte. The concentration of Cd^{2+} ions was maintained at a constant level from the first stages of dissolution, while the amounts of Ni^{2+} and Fe^{3+} increased gradually over time. It seems that a residence time of 0.5 h was enough to achieve the complete dissolution of the phases containing cadmium, i.e. the anode and the active electrode materials, but not the cathode with iron as a main constituent. Addition of H_2O_2 (at once or periodically) enhanced the dissolution of the cathode, hence the increased concentrations of Fe^{3+} and Ni^{2+} ions in the solution.

Hydrogen peroxide improved the dissolution of nickel, but also increased the dissolution of iron necessitating further treatment of the solution. The dissolution of the material from the spent batteries was incomplete and some of solids remained after the process. The solid residues were washed, the scraps of the electrodes (i.e. the metallic pieces visible to the naked eye) were separated from the "powder", dissolved in HNO_3 and analysed. Table 4 shows the composition of the liquor solution and the solid residues.

It was found that 80–100% of cadmium and over 73% of nickel were able to dissolve from the Ni–Cd battery. Among the three metals, cadmium was the element which could dissolve most readily. These

Table 3
Content of metals in Ni–Cd battery and its components

Component		Content, wt.%	
		B-1	B-2
Battery (total)	Ni	24.32	26.40
	Cd	33.17	34.20
	Fe	12.92	12.57
Anode [a]	Ni	1.86	1.24
	Cd	60.02	69.91
	Fe	28.75	27.70
Cathode [a]	Ni	35.76	38.25
	Cd	2.48	3.50
	Fe	60.43	50.45
Active materials	Ni	34.97	38.28
	Cd	28.25	28.02
	Fe	0.14	0.27
Residues on separators	Ni	4.72	4.73
	Cd	28.69	31.06
	Fe	0.13	0.14

[a] The plaques were not cleaned chemically from the active electrode material strongly adhered to the electrode surface.
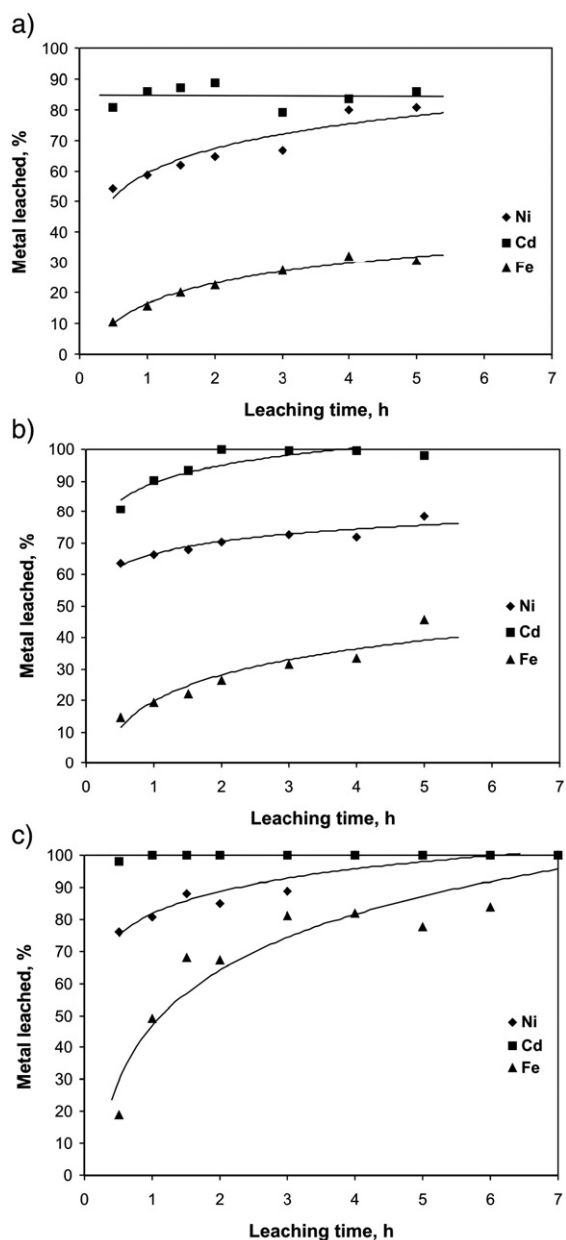
a)

b)

c)

Fig. 2. The influence of H_2O_2 dosage on percentage of metal leached: a) no H_2O_2 addition, b) 5 cm^3 H_2O_2 added at the beginning of the leaching, c) 110 cm^3 H_2O_2 added periodically.

results are consistent with the data reported by Pietrelli et al. (2005). More than 50% of iron was transferred from the solid phase into the solution doped with H_2O_2.

It was found that after 5 h of the leaching, the liquor solution contained usually 9–11 g/dm^3 Ni^{2+}, 9–11 g/dm^3 Cd^{2+} and up to 3.5 g/dm^3 Fe^{3+}. Insoluble "powder" contained mainly nickel (over 53%) and cadmium (ca. 40%), while the residues of the electrode scraps consisted of iron (over 70%) and nickel (20–30%).

Table 4
Content of metals in the leaching solution and the solid residues

Series	Composition			
	Metal	Solution	Solid residue, wt.%	
		g/dm^3	"Powder"	Metallic scraps
B-1				
L-I	Ni	12.949	58.7	26.2
	Cd	8.912	35.8	1.0
	Fe	1.579	5.5	72.8
L-II	Ni	11.174	85.9	21.9
	Cd	11.317	7.9	0.8
	Fe	3.371	6.2	77.3
L-III	Ni	11.264	0	0
	Cd	9.173	0	0
	Fe	5.057	0	0
B-2				
L-II	Ni	8.810	99.7	2.5
	Cd	12.702	0.1	0.1
	Fe	3.450	0.2	97.4
L-III	Ni	10.706	53.2	29.1
	Cd	10.630	45.9	0.8
	Fe	3.148	0.9	70.1

The detailed compositions of the Ni–Cd batteries were determined according the leaching data (Table 5). The results confirmed the previous analysis. The AA cells contained 32.1±2.9% Ni, 36.7±2.0% Cd, 11.6±2.9% Fe and 29.8±4.0% of the other elements (not analyzed here in details, e.g.: K, O, H from hydroxides).

3.3. Electrowinning

Electrowinning was undertaken using the leach solution. The variable parameters were pH and cathodic current density. Samples of the electrolyte were taken during the electrolysis and analyzed for Cd^{2+}, Ni^{2+} and Fe^{3+}. Fig. 3 shows the changes of the concentrations of the ions with time.

Table 5
Mean composition of the Ni-Cd cells

Series	Content, wt.%			
	Ni	Cd	Fe	Other elements
B-1				
L-I	35.8	23.6	6.9	34.0
L-II	31.4	26.6	13.4	29.0
L-III	33.4	29.7	13.7	26.0
B-2				
L-II	27.9	27.5	10.9	34.0
L-III	32.1	29.2	13.3	26.0

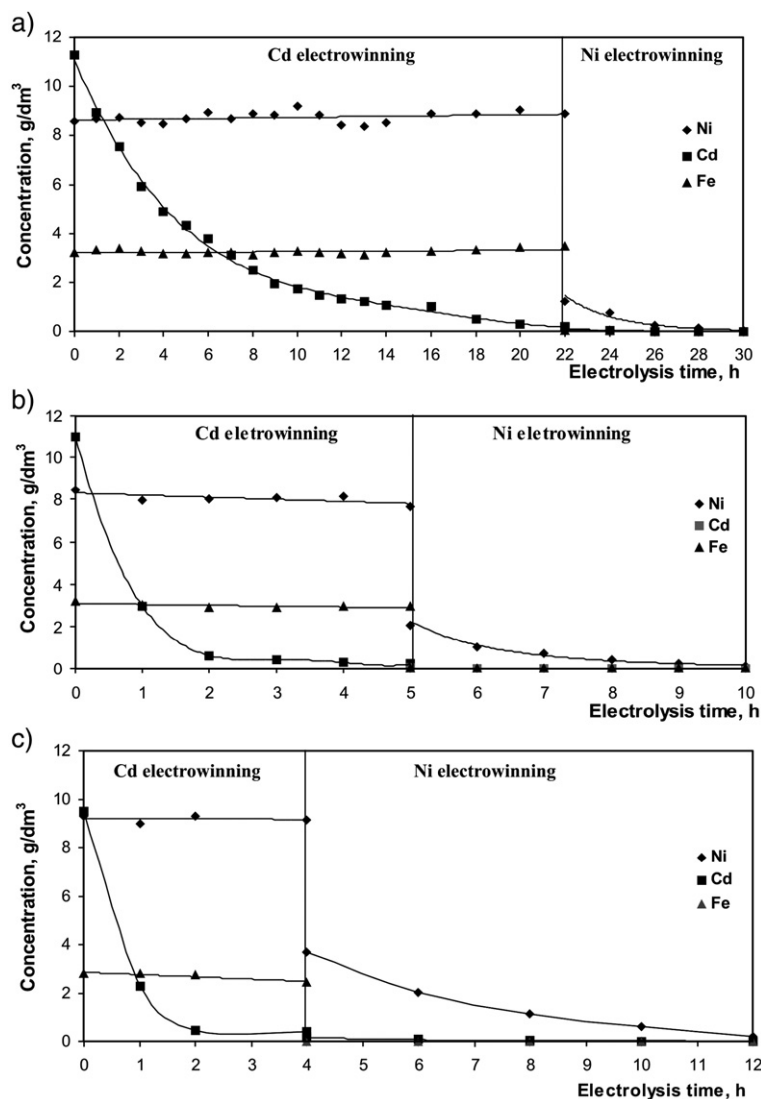Fig. 3. The influence of the electrolysis time and the current density on Ni^{2+}, Cd^{2+} and Fe^{3+} concentrations in the solution: a) series E-I, b) series E-II, c) series E-III.

During the process, the concentration of Cd^{2+} ions in the acidic solutions decreased gradually, while the concentrations of Ni^{2+} and Fe^{3+} ions remained almost constant. Various current densities did not affect the concentration-time dependence. The recovery of cadmium was completed in 5 h at 400 A/m^2 (E-II) instead of 22 h at 100 A/m^2 (E-I). The highest drops of the Cd^{2+} concentration were observed at the beginning of the electrolysis, while at longer times the mass decrements decreased gradually. The change of the current density did not affect the concentrations of Ni^{2+} and Fe^{3+} ions in the bath. Increasing the pH of the solution from natural (E-III) to 1 (E-II) had no practical influence on the cadmium electrowinning.

The initial concentration of Cd^{2+} ions in the solution was dependent on the composition of the sample used in the leaching stage. After complete cadmium electrowinning the concentration of Cd^{2+} in the bath decreased usually from about 11 g/dm^3 to about 0.2 g/dm^3, >98% recovery.

After cadmium recovery, the remaining electrolyte had its pH raised to 3–4 and ferric ions hydrolysed and $Fe(OH)_3$ precipitated in the bulk of the solution. The precipitation was accompanied by a decrease in the Ni^{2+} concentration in the solution. Nickel losses visible in Fig. 3 (at the beginning of the Ni electrowinning stage) were caused by both coprecipitation with iron hydroxide (0.05–0.35 g) and increasing the volume of the solution
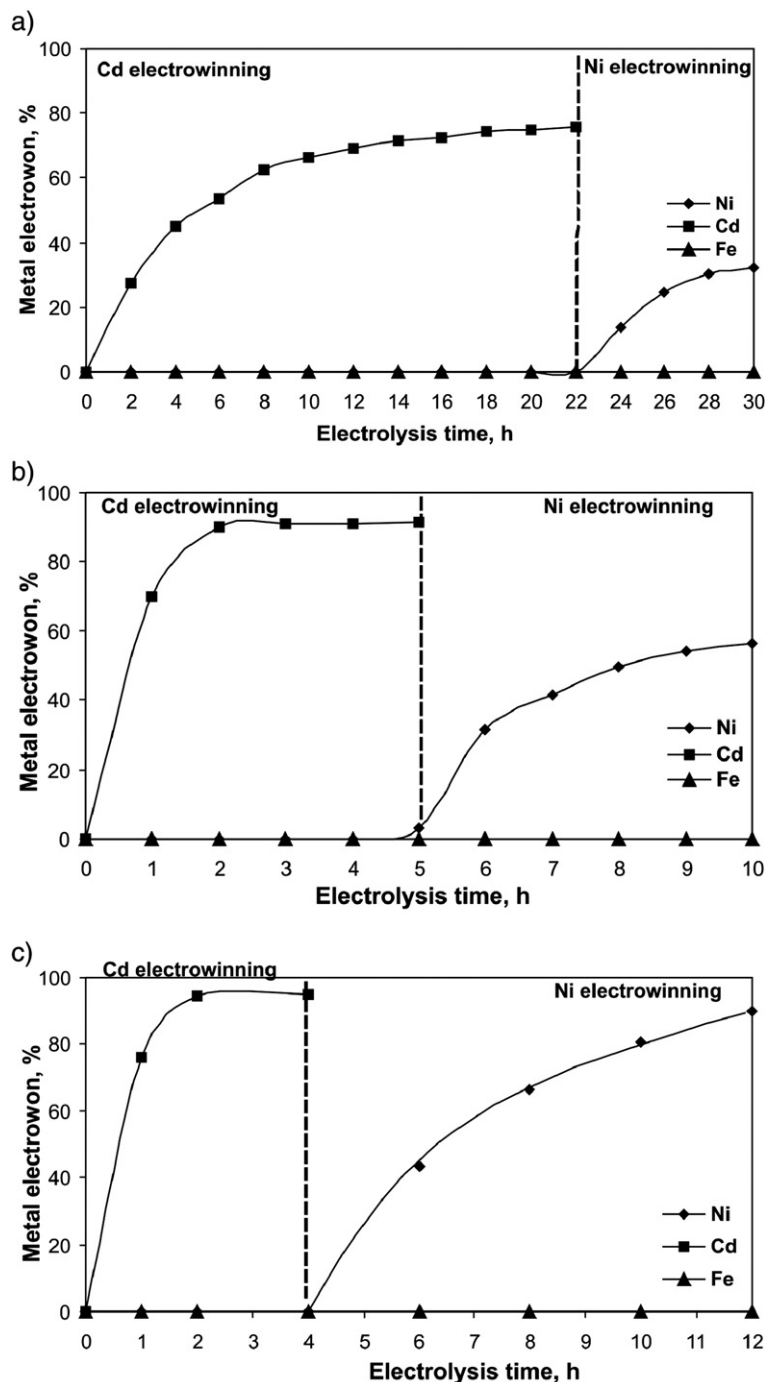
Fig. 4. The influence of the electrolysis time and the current density on the percentage electrowon metals: a) series E-I, b) series E-II, c) series E-III.

by adding ammonia solution (from 0.2 dm^3 to 0.5 or 1 dm^3). The volume of SOLUTION C was not reduced (by evaporation), since at high concentrations of both SO_4^{2-} and Na^+ ions Na_2SO_4 readily crystallizes from solution. The solution was then raised to pH 9 with ammonia and the iron precipitate filtered.

Nickel electrowinning was carried out from ammoniacal solutions at current densities of 100 and 400 A/m^2. The main component of these solutions were Ni^{2+}-ammonia complex ions, while total amount of Cd^{2+} and Fe^{3+} did not exceed 0.01 g/dm^3. During the electrolysis, the decrease in the concentrations of all ions, though
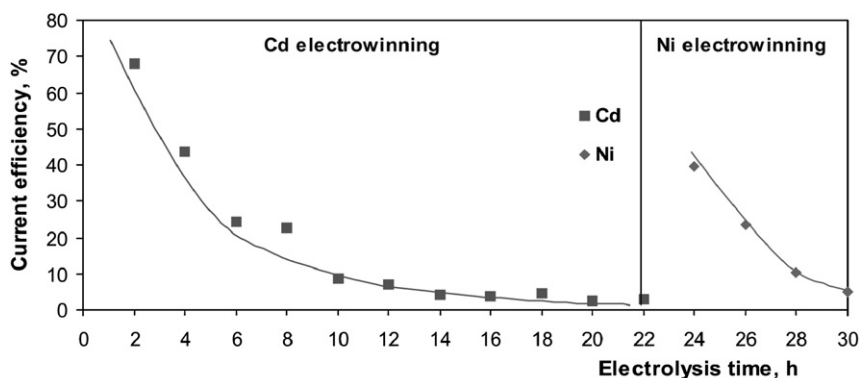
Fig. 5. The influence of electrolysis time on the cathodic current efficiency — series E-I.

especially of nickel, was observed. Nickel recovery was achieved in 5 h at 400 A/m^2 and 8 h at 100 A/m^2. The total time of the electrolysis depended also on the initial concentration of Ni^{2+} ions in the bath.

At each electrolysis stage the mass of the cathodic deposit was determined. It was found that at longer times the mass increments became lower. The highest metal recovery during cadmium electrowinning at 100 A/m^2 was achieved in two initial stages with total time of 4 h. At higher current density the considerable mass increment was observed only at the first stage (after 1 h). The change of pH of the solution did not significantly affect the recovery of cadmium.

Fig. 4 shows the influence of the electrolysis time on the percentage of the individual metals deposited on the cathode. At initial stages only cadmium ions were reduced in the cathodic process, while Ni^{2+} and Fe^{3+} ions remained in the bath. It was consistent with the previously reported results. At lower current density the mass of the cathodic deposit remained unchanged for

times longer than 14 h, while at higher current density almost 96% of cadmium was recovered within 2 h.

Chemical analysis of the cathodic deposits confirmed that only cadmium deposited from the acidic solution. At 100 A/m^2 the cathodic deposits consisted of 99.4–99.99% of cadmium, but at 400 A/m^2 the purity decreased to 94–98% Cd. Nickel was detected in the spongy deposits and it seems that the contamination of cadmium resulted mainly from the occlusion of the electrolyte within the pores of the deposit. Increasing the solution pH from natural to 1 did not significantly change the purity of the cathodic deposits. The nickel electrodeposits were 98–99% Ni, since the traces of the cadmium ions were still present in the bath.

Cadmium deposited in the form of grey, matt, rather spongy metal, while the nickel deposits were grey and bright, but they peeled off already during the electrolysis indicating highly stressed metal.

Current efficiencies based on the mass increments of the cathodes from the electrolyser and the copper coulometer were calculated. Fig. 5 shows that the current efficiency
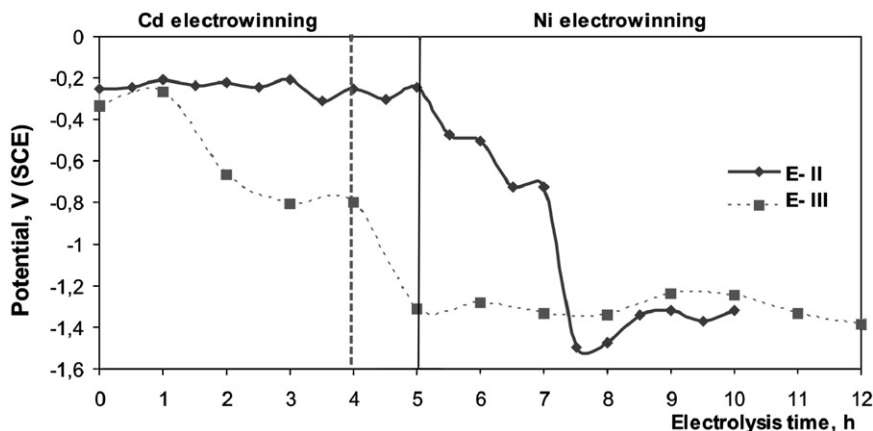

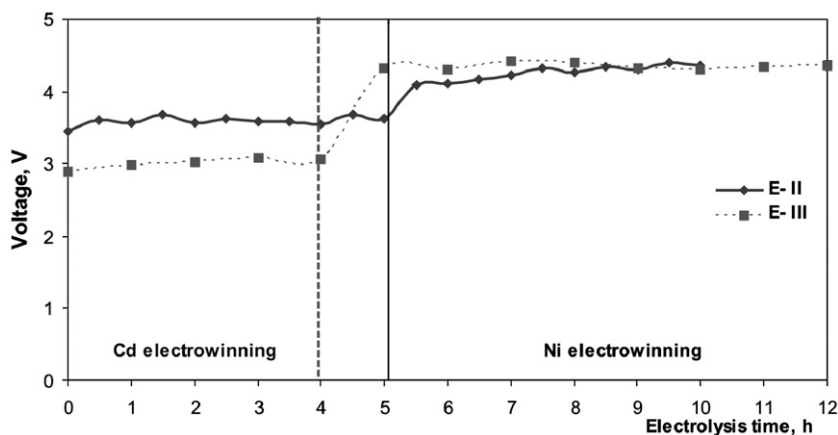Fig. 6. Changes of the cathode potential within the electrolysis time at the current density of 400 A/m^2.

Fig. 7. Changes of the electrolysis voltage with the electrolysis time at the current density of 400 A/m^2.

decreased with the time. It is obvious, since the concentration of the metal ions also decreased. The efficiency reached a maximum of 70% in the initial stages of cadmium electrowinning, but decreased gradually to 0.2–0.5%. At 400 A/m^2, the current efficiency decreased to zero within 3–4 h. An increase in the pH from natural to 1 led to an decrease in the maximum efficiency to about 55%. The efficiency for the nickel electrowinning was 30–40% at the beginning of the process. At higher current density the efficiency of the electrolysis was lower at about 10%.

The potential of the cathode was monitored during the electrolysis. These measurements seem to be very useful for determining the end of the cadmium electrowinning stage. Fig. 6 shows the changes of the potential recorded at the current density of 400 A/m^2. It was found that cadmium deposits at potential higher than for nickel. The potential reached values of about −0.25 V (SCE) for the electrolyte at pH=1. In more acidic solution the reduction of hydrogen ions was enhanced and, hence, the

cathode potential decreased gradually to −0.8 V (SCE) with the decreasing in the Cd^{2+} concentration. The electrodeposition of nickel occurred at the potentials of about −1.2 V. Such low values resulted from both low Ni^{2+} concentrations in the bath and high cathodic overpotential characteristic of nickel deposition.

The voltage of the electrolysis was controlled (Fig. 7). It was maintained at 3.0–3.5 V during cadmium recovery, while at the nickel electrowinning the voltage was higher by about 0.5 V. Decreasing the pH for cadmium electrowinning led to an increase in the solution conductivity and, consequently, to a lower electrolysis voltage.

The consumption of the energy Z on the mass unit of the deposited metal (m_d) was calculated:

$$Z = \frac{U \cdot I \cdot t}{m_d} \tag{1}$$

where

U	voltage of the electrolysis
I	current intensity
t	duration of the electrolysis stage

The results are presented in Fig. 8. It was found that the consumption of the energy increased with the electrolysis time from about 2–2.5 kW h/kg to about 600 kW h/kg for cadmium and from 6–14 kW h/kg to 50–160 kW h/kg for nickel. High values of the consumed energy corresponded to the low concentrations of the recovered metals in the solution and, hence, low current efficiencies of the cathodic process.

3.4. Mass balance

Total balance for cadmium and nickel recovered in the electrolysis stages was determined. The amounts of
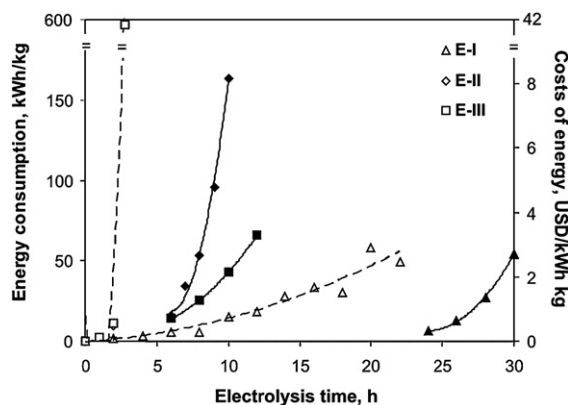

Fig. 8. Changes of the energy consumption and costs of the energy with the electrolysis time (white points — Cd electrowinning, black points — Ni electrowinning).

Cd^{2+}, Ni^{2+} and Fe^{3+} ions in the initial solutions (200 cm^3) were assumed as 100%. It was calculated that about 70% and over 91% of cadmium was recovered at the current densities of 100 A/m^2 and 400 A/m^2, respectively. Maximum recovery of nickel was about 89% at 400 A/m^2.

The losses of metals were caused mainly by withdrawing solution samples during the electrolysis. At cadmium electrowinning stage, the sampling led to the losses of both cadmium and nickel ions, whereas 2.5–5.5% of nickel ions were coprecipitated with iron. The results presented in Table 6 show that 100% recovery was unachievable.

The total recovery of cadmium and nickel from the Ni–Cd batteries was also estimated. The efficiencies of both leaching and electrolysis stages were taken into considerations. The amounts of the metals taken out of the bath during sampling were assumed as recovered. The results of the calculations are listed in Table 7. Maximum total recoveries of cadmium and nickel were 92% and 67%, respectively.

3.5. Economic viability

An economic viability of the proposed process was assessed. This evaluation is rather qualitative, since solely main costs of the reagents and the energy consumed during electrolysis were taken under consideration. It was estimated that 1.5 t of spent Ni–Cd batteries corresponds to 1 t leachable material (the batteries without the external cases). At contents of metals 34% Cd and 25% Ni in the

Table 6
Balance of recovery and losses of metals

Series	Stage		Distribution, %		
			Ni	Cd	Fe
Initial solution			100	100	100
E-I	Cd electrowinning	Cathode	0.08	75.87	0.09
		Losses	47.01	11.78	46.46
	Fe removal		5.65	0.36	44.34
	Ni electrowinning	Cathode	32.28	0.18	0.01
		Losses	0.73	0.13	0.07
	Final solution		1.56	0.12	0.55
E-II	Cd electrowinning	Cathode	3.23	91.53	0.15
		Losses	2.89	0.70	2.84
	Fe removal		20.82	0.36	74.55
	Ni electrowinning	Cathode	52.94	0.66	0.10
		Losses	0.28	0	0
	Final solution		3.66	0	0
E-III	Cd electrowinning	Cathode	0.07	94.99	0.16
		Losses	1.84	0.67	1.92
	Fe removal		2.39	0.49	86.59
	Ni electrowinning	Cathode	89.27	0.05	0.05
		Losses	0.38	0.02	0.01
	Final solution		4.93	0.57	0.68

Table 7
Total recovery of Cd and Ni

Series	Metal	Leaching efficiency %	Current efficiency, % (cathode+sampling)	Total recovery (estimated) %
E-I	Cd	100	87.65	87.65
	Ni	73	80.02	58.41
E-II	Cd	100	92.23	92.23
	Ni	73	56.11	40.96
E-III	Cd	81	95.66	77.48
	Ni	73	91.49	66.79

spent battery and maximum total recoveries of 92% Cd and 67% Ni, about 315 kg Cd and 165 kg Ni are recoverable. The costs of the leaching with sulphuric acid (s:l ≈ 1:30 w/w, i.e. 25 m^3 20% H$_2$SO$_4$ per 1 t of leached material) represent about 300 USD (55 USD/Mg of concentrated H$_2$SO$_4$ (Boyd, 2006)). At actual prices of ammonia and sodium hydroxide necessary for iron removal, the cost of the reagents can increase to 1000 USD. Assuming 0.07 USD/kW h (the average energy price in EU is 50–55 €/MW h (EU, 2006)), the costs borne for the energy consumed for metals electrowinning (for maximum values of 50–100 kW h/kg; Fig. 8) are 1500–3000 USD. This value was estimated for the electrolysis stages with the current efficiencies higher than 10%, since these conditions seem to be most reasonable for conducting the process. Finally, the total cost of the recycling process (315 kg Cd, 165 kg Ni) is not less than 2500–4000 USD per 1.5 t of spent Ni–Cd batteries. The results were compared with the actual prices of cadmium and nickel of similar quality. These are about 5 USD/kg Cd (MP, 2007) and 45 USD/kg Ni (LME, 2007). Therefore the cost of the equivalent amounts of recovered metals (315 kg Cd, 165 kg Ni) is approximately 9000 USD. The hydrometallurgical recovery of cadmium and nickel from spent Ni–Cd batteries seems rather beneficial, even though not all of the economic factors (e.g. the costs of the disassembly, waste disposal etc.) were taken into account in the rough calculations given above.

4. Conclusions

The studies presented in this paper showed that high degree of recovery of cadmium and nickel is achievable by the hydrometallurgical treatment of spent Ni–Cd batteries. The process consisted of the following stages: leaching in hot H$_2$SO$_4$ (with H$_2$O$_2$ addition), cadmium electrowinning, Fe(OH)$_3$ precipitation, nickel electrowinning. The final products were metals with high purity. High losses of nickel can result from the iron hydroxide precipitation. However, the removal of Fe^{3+} from the solution is necessary to provide subsequent nickel recovery.

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